Electrical conductivity of CaSO4 in aqueous solution under high pressure

AUTHOR(S):

Inada, Etsuko; Shimizu, Kiyoshi; Osugi, Jiro

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, Vol. 42, No. 1, 1972

ELECTRICAL CONDUCTIVITY OF $CaSO_4$ IN AQUEOUS SOLUTION UNDER HIGH PRESSURE

BY ETSUKO INADA, KIYOSHI SHIMIZU* AND JIRO OSUGI

The electrical conductivity of aqueous solutions of 2–2 electrolytes, $CaSO_4$ and $MgSO_4$, has been measured within the ranges, 15~40°C, 1~1,200kg/cm^2 and 10^{-3}~10^{-4} M. The plots of Λ *vs* $C^{1/2}$ under high pressure show Kohlraush's linear relation in this concentration range. The equivalent conductance at infinite dilution Λ° has a maximum against pressure. The pressure at this maximum point has been found to be higher than that of the minimum viscosity of water at each temperature. The hydration numbers of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions calculated by the Robinson-Stokes method are little changed by pressure and/or temperature. The dissociation constants of Ca^{2+}·SO_4^{2-} and Mg^{2+}·SO_4^{2-} ion-pairs are increased by pressure and decreased by temperature. The thermodynamic parameters, $\Delta\bar{G}^\circ$, $\Delta\bar{V}^\circ$, $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$, are calculated from the coefficients of pressure and temperature of the dissociation constants. The closest approach distances of the ion-pairs are also estimated by using the theoretical equation of Fuoss. These ion-pairs would be solvent-separated ones, containing some water molecules between the cation and anion, and approach contact ones, liberating the water molecules with increasing temperature.

Introduction

From the measurements of the conductances of electrolytes, the information on the behaviors of both free ions and ion-pair is obtained. The limiting equivalent conductance Λ°, which is specific to the individual ions, is an important quantity to study the ion-solvent interaction. In order to know the effect of pressure on the solvation of ions, we have determined the values of Λ° of 2-2 electrolytes under high pressure.

The dissociation constants of the ion-pairs have been obtained under high pressure for many electrolytes in water. Many of them increase as pressure increases [1], but some decrease or remain constant [2]. The molecular structures of the ion-pairs in aqueous solution have been examined with many different techniques [3,4], which has suggested that the association of divalent metal sulphates would take place through two or more interposed water molecules. However, the effect of pressure on the structure of the ion-pair was elucidated only in the case of $[Co(NH_3)_6]^{3+}$·SO_4^{2-} [5].

(*Received April 30, 1972*)

* Present address: *Department of Applied Chemistry, Faculty of Technology, Doshisha University, Kyoto*

1) S. D. Hamann, P. J. Pearson and W. Strauss, *J. Phys. Chem.*, **68**, 375 (1964)
2) J. F. Skinner and R. M. Fuoss, *ibid.*, **70**, 1426 (1966)
3) R. Larsson, *Acta Chem. Scand.*, **18**, 1923 (1964)
4) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 93, 108 (1962)
5) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 12 (1970)

In this paper, the pressure and temperature effects on hydration numbers of free ions and the structures of the ion-pairs of the 2-2 electrolytes, $CaSO_4$ and $MgSO_4$, in water have been examined up to 1,200 kg/cm^2 at the temperatures of 15, 25 and 40°C.

Experimental

The conductivity cell used for high pressures was a syringe-type cell of glass and platinum, as shown in Fig. 1 (a). The oil pressure in the pressure vessel was transmitted to the sample solution by the glass piston of the syringe. The platinum electrodes in the cell were lightly coated with platinum black to avoid polarization. The cell constant K_{cell} was determined by aqueous KCl solution of 10^{-2}N [6]. The pressure-generating apparatus is shown in Fig. 1 (b). The Bourdon-type gauge was calibrated with a free piston-type gauge. The resistance R was measured by the Yanagimoto MY-7-type a.c. bridge.

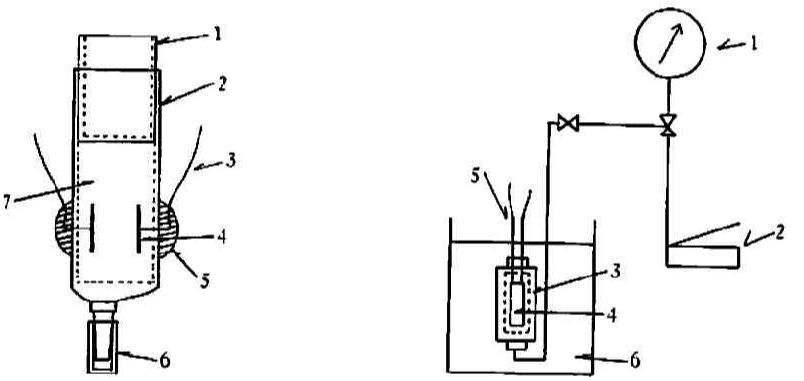

Fig. 1 Experimental apparatus

(a) High pressure conductivity cell
1: Glass piston
2: Glass cylinder
3: Leading wire
4: Platinum electrode
5: Araldite
6: Teflon capsule
7: Sample solution

(b) Pressure-generating apparatus
1: Bourdon-type pressure gauge
2: Hand pump
3: High pressure vessel
4: High pressure conductivity cell
5: Leading wire
6: Paraffin oil bath

The conductivity water was repeatedly distilled and in equilibrium with air. The $1{,}000 \times 10^{-3}$M stock solutions of $CaSO_4$ and $MgSO_4$ were prepared from the analytical grade reagents. The solutions in the concentration range of $10^{-4} \sim 10^{-3}$M were prepared by diluting the stock solutions with the conductivity water. The concentrations of these dilute solutions at high pressure were corrected with the volume of water at the corresponding pressure calculated by the Tait equation [7],

6) G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, 13, 473 (1945)
7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold, New York (1958)

$$\frac{V^{(1)}-V^{(P)}}{V^{(P)}}=C\log\frac{B+P}{B+1}. \quad (1)$$

where B and C are the characteristic parameters of water.

The specific conductivity of the solution κ is defined by Eq. (2),

$$\kappa=\frac{K_{cell}}{R}. \quad (2)$$

By subtracting from κ the specific conductivity of water κ° (at 25°C, 1.19×10^{-6}ohm^{-1}cm^{-1} at 1 atm and 1.94×10^{-6}ohm^{-1}cm^{-1} at 1,200 kg/cm^2), the equivalent conductance Λ is obtained by Eq. (3),

$$\Lambda=\frac{1000(\kappa-\kappa^\circ)}{C}, \quad (3)$$

where C is the corrected equivalent concentration.

Results and Consideration

Pressure dependence of Λ

The plots of Λ against $C^{1/2}$ have Kohlrausch's linear relation at each pressure and temperature, as shown in Fig. 2. The limiting equivalent conductance Λ° is determined by the extrapolation of the $\Lambda\sim C^{1/2}$ curve to zero concentration. Table 1 shows the values of Λ and Λ° obtained at each concentration, temperature and pressure. The pressure dependence of Λ is shown in Fig. 3, where an up-

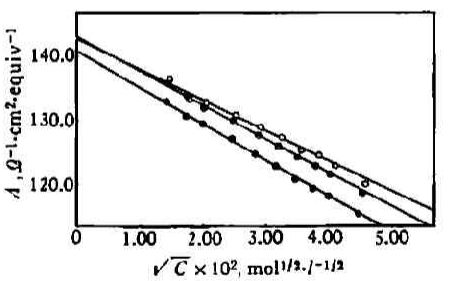

Fig. 2 Λ vs $\sqrt{C}$ ($CaSO_4$, 25°C)
●: 1 atm
◓: 600 kg/cm²
○: 1,200 kg/cm²

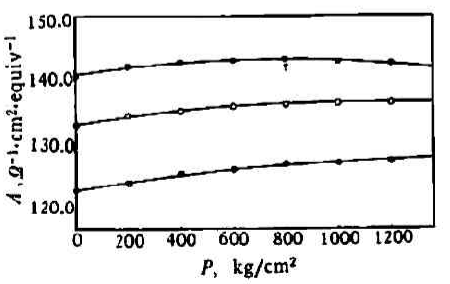

Fig. 3 Λ vs P ($CaSO_4$, 25°C)
●: C→O, ○: $C^{(1)}=2.000\times10^{-4}$N
◓: $C^{(1)}=1.000\times10^{-3}$N

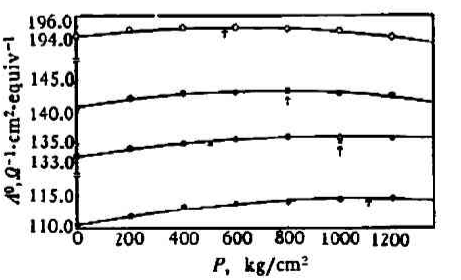

Fig. 4 Λ° vs P
●: $CaSO_4$, 15°C, ◓: $CaSO_4$, 25°C
○: $CaSO_4$, 40°C, ◒: $MgSO_4$, 25°C
×: Fisher's value

arrow, ↑ indicates the maximum point of Λ. The maximum of Λ shifts to a higher pressure as the concentration increases. The pressure dependence of Λ° at each temperature is shown in Fig. 4. The

Table 1 Λ and Λ^0 ($\Omega^{-1}\cdot cm^2\cdot equiv^{-1}$)

(a) Aqueous solution of $CaSO_4$ (15°C)

Pressure \ $M\times10^4$	1.000	2.000	3.000	4.000	5.000	6.000	8.000	10.00	Λ^*
1 atm	105.0	102.1	100.3	98.7	97.1	95.5	92.9	90.2	110.4
200 kg/cm²	107.1	103.9	102.2	100.4	99.2	97.5	95.1	92.4	111.8
400	108.3	105.5	103.6	102.2	100.8	99.0	96.5	93.7	113.2
600	109.5	105.9	104.2	102.7	101.5	100.0	97.6	94.9	113.8
800	109.9	106.6	104.9	103.7	102.2	100.5	99.4	95.7	114.0
1,000	110.4	107.1	105.4	104.2	102.8	101.0	99.1	96.1	114.4
2,000	111.0	107.5	105.9	104.5	103.4	101.5	99.6	96.6	114.6

(b) Aqueous solution of $CaSO_4$ (25°C)

Pressure \ $M\times10^4$	1.000	1.500	2.000	3.000	4.000	5.000	6.000	7.000	8.000	10.00	Λ^*
1 atm	133.1	130.8	129.5	127.3	124.9	122.9	120.9	119.5	118.1	115.3	140.7
200 kg/cm²	134.5	132.5	130.8	128.6	126.1	124.0	122.2	120.9	119.3	116.2	142.1
400	135.2	133.4	131.7	129.3	126.3	125.3	123.5	122.1	120.1	117.4	142.7
600	135.8	133.8	132.2	130.0	127.8	126.1	124.3	123.0	121.6	118.6	143.0
800	136.1	133.5	132.7	130.6	128.5	126.9	125.0	123.6	122.1	119.4	143.2
1,000	136.3	133.5	132.9	130.9	128.7	127.0	125.4	124.2	122.7	120.1	142.9
1,200	136.4	133.4	132.9	131.0	129.1	127.3	125.5	124.3	122.9	120.1	142.6

(c) Aqueous solution of $CaSO_4^{\pm}$(40°C)

Pressure \ $M\times10^4$	1.500	2.000	2.500	3.000	4.000	5.000	Λ^*
1 atm	178.4	176.1	173.8	171.9	168.1	165.2	194.6
200 kg/cm²	179.7	177.5	175.6	173.5	169.8	166.9	195.6
400	179.7	178.0	176.0	173.5	170.6	167.2	195.8
600	179.9	178.2	176.2	174.1	171.0	167.9	195.8
800	179.8	178.2	176.3	174.2	171.3	168.0	195.6
1,000	179.5	178.1	176.2	174.2	171.3	168.1	195.3
1,200	179.2	177.9	175.9	174.0	171.7	168.1	194.4

(d) Aqueous solution of $MgSO_4$ (25°C)

Pressure \ $M\times10^4$	2.000	2.500	3.000	3.500	4.000	5.000	Λ^*
1 atm	123.5	121.5	120.7	119.2	118.0	116.5	133.1
200 kg/cm²	124.8	123.4	122.2	121.2	120.4	118.5	134.4
400	125.3	124.6	123.3	122.3	121.4	118.8	135.0
600	126.2	125.3	123.9	123.2	122.1	119.6	135.8
800	126.5	135.6	124.1	123.4	122.4	120.1	136.0
1,000	126.8	126.1	124.3	123.6	122.6	120.3	136.0
1,200	126.9	125.8	124.7	124.0	122.5	120.4	136.0

pressure of the maximum Λ°, $P(\Lambda^\circ)$ shifts to a lower pressure as temperature increases, and $P(\Lambda^\circ)$ of $CaSO_4$ is lower than that of $MgSO_4$ at 25°C.

Now, in the case of the dissociation of the symmetrical electrolyte ($z_+=|z_-|$) into its free ions, the specific conductivity of the electrolyte, $\kappa-\kappa^\circ$, is given by Eq. (4),

$$10^3(\kappa-\kappa^\circ)=\sum C_i\lambda_i=C\alpha\sum\lambda_i\,. \tag{4}$$

where C_i and λ_i are the equivalent concentration and equivalent conductance of i-ion, respectively and α the degree of dissociation. From Eqs. (3) and (4),

$$\Lambda=\alpha\sum\lambda_i\,, \tag{5}$$

that is, the equivalent conductance is proportional to the degree of dissociation and the sum of the ionic conductances. Therefore, the shift of $P(\Lambda)$, the pressure of the maximum Λ, to a higher pressure with the increase of the concentration is ascribed to the fact that the pressure coefficient of α is more effective for Λ in the lower dilute solution than in the higher.

The pressure dependence of Λ° would be explained qualitatively by Stokes' law,

$$\lambda^\circ_i=\frac{|z_i|eF}{6\pi r_i\eta^\circ}\,, \tag{6}$$

where λ°_i, z_i and r_i are the limiting ionic equivalent conductance of i-ion, its ionic valence and its Stokes radius, respectively, and F the Faraday constant, e the electronic charge, and η° the viscosity of water. The viscosity of water has a minimum against pressure at lower temperatures, because the structure of water would be broken down by pressure. The minimum point disappears at about 36°C [8~10], above which the viscosity increases monotonously with increasing pressure. The pressures at the minimum η°, $P(\eta^\circ)$ are 950 kg/cm² at 15°C and 600 kg/cm² at 25°C [11]. When the hydrated ion with the constant effective radius migrates in a continuous medium whose viscosity is η° under pressure, $P(\Lambda^\circ)$ should be equal to $P(\eta^\circ)$ according to Eq. (6). As shown in Fig. 4, this is not the case; $P(\Lambda^\circ)$ is higher than $P(\eta^\circ)$ at each temperature. The maximum point of Λ° is found even at 40°C, where the viscosity of water increases monotonously with increasing pressure. These discrepancies would be explained from the view point of the decrease in the radius of the hydrated ion by pressure according to the Robinson-Stokes method[12], though there have been other standpoints of the local viscosity in the vicinity of the ion[13] and of the effect of dielectric relaxation on ionic motion [2,14,15].

Hydration numbers of the free ions

8) L. Hauser, *Ann. Phys.*, 5, 597 (1901)
9) E. M. Stanley and R. C. Batten, *J. Phys. Chem.*, 73, 1187 (1969)
10) K. E. Bett and J. B. Cappi, *Nature*, 207, 620 (1965)
11) J. B. Cappi, Ph. D. Thesis, London University (1964)
12) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, 40, 1 (1970)
13) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, 70, 2325 (1966)
14) R. Zwanzig, *J. Chem. Phys.*, 38, 1603 (1963)
15) R. Fernandez-Prini and G. Atkinson, *J. Phys. Chem.*, 75, 239 (1971)

The Robinson-Stokes method [16] has been applied to calculate the hydration number of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions under high pressure as follows [12].

$$\lambda_{i(P)}=\Lambda^{\circ}_{(P)}\cdot t^{\circ}_{i(P)}, \tag{7}$$

where $t^{\circ}_{i(P)}$ is the limiting transference number of i-ion at pressure P. It is assumed that $t^{\circ}_{i(P)}=t^{\circ}_{i(1)}$. The values of the cationic transference number are as follows,

$$t^{\circ}_{+(P)}=t^{\circ}_{+(1)}=\frac{\lambda^{\circ}_{+(1)}}{\Lambda^{\circ}_{(1)}}, \quad \left.\begin{array}{ll} 0.427 \text{ at } 15^{\circ}C \\ 0.426 \quad 25^{\circ}C \\ 0.419 \quad 40^{\circ}C \end{array}\right\} Ca^{2+}, \quad 0.399 \quad 25^{\circ}C \quad Mg^{2+} \tag{8}$$

where $\lambda^{\circ}_{(1)}$ were cited from the literatures [16,17]. From Eqs. (6) and (7), the Stokes radius r_i is obtained. Introducing the correction factor $f_{R\text{-}S}$ for r_i, the effective radius of hydrated ion r_e is obtained. The volume of the hydration sheath in the neighborhood of the ion is

$$V_A=\frac{4}{3}\pi(r_e^3-r_c^3), \tag{9}$$

where r_c is the crystal radius of i-ion. Then the hydration number is given by the equation,

$$h=\frac{V_A}{V_W}, \tag{10}$$

where V_W is the average volume of one water molecule in the hydration sheath and was assumed to be equal to that of the bulk water at each pressure. These numerical values of λ°_i, $f_{R\text{-}S}$, r_e and h are listed in Table 2. As shown in Table 2, the hydration numbers of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions are invariant within the experimental error as temperature increases. Also, the hydration numbers of these ions are little changed by pressure as in the case of $[Co(NH_3)_6]^{3+}$ and SO_4^{2-} ions[12]. This is not in agreement with Horne's opinion of the dehydration of ions by pressure[18].

Dissociation of the ion-pairs

The ion-pairs of $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$ would be in equilibrium with their free ions,

$$\underset{m(1-\alpha)}{M^{2+}\cdot SO_4^{2-}} \rightleftharpoons \underset{m\alpha}{M^{2+}}+\underset{m\alpha}{SO_4^{2-}}, \tag{11}$$

where M^{2+} represents the metal ion and m is the stoichiometric molar concentration. Then the dissociation constant K in the system of Eq. (11) is defined as follows,

$$K=\frac{m\alpha^2}{(1-\alpha)}\cdot\frac{f_1 f_2}{f_3}, \tag{12}$$

16) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths Scientific Publications, London (1965)

17) A. G. Keenan, H. C. Mcleod and A. R. Gordon, *J. Chem. Phys.*, **13**, 466 (1965)

18) R. A. Horne, "Advances in High Pressure Research", Vol. 2, Chap. 3, ed. by R. S. Bradley, Academic Press, London (1969)

Table 2 λ°_i, $f_{R\text{-}S}$, r_e, h and V_W

(a) $CaSO_4$ (15°C)

Pressure	Ca^{2+} $r_e=0.99$Å				SO_4^{2-} $r_e=2.73$Å				V_W (Å^3)
	λ°_i	$f_{R\text{-}S}$	r_e (Å)	h	λ°_i	$f_{R\text{-}S}$	r_e (Å)	h	
1 atm	47.1	1.36	4.09	9.4	63.3	1.62	3.63	3.8	30.0
200 kg/cm^2	47.7	1.36	4.09	9.5	64.1	1.62	3.63	3.9	29.8
400	48.3	1.36	4.08	9.5	64.9	1.62	3.61	3.8	29.5
600	48.6	1.36	4.08	9.6	65.2	1.62	3.61	3.8	29.3
800	48.7	1.36	4.08	9.7	65.3	1.62	3.63	4.0	29.0
1,000	48.8	1.36	4.08	9.7	65.6	1.62	3.61	3.9	28.8
1,200	48.9	1.37	4.08	9.8	65.7	1.62	3.60	3.9	28.6

(b) $CaSO_4$ (25°C)

Pressure	Ca^{2+}				SO_4^{2-}				V_W (Å^3)
	λ°_i	$f_{R\text{-}S}$	r_e (Å)	h	λ°_i	$f_{R\text{-}S}$	r_e (Å)	h	
1 atm	59.9	1.35	4.10	9.5	80.8	1.61	3.64	3.9	30.0
200 kg/cm^2	60.5	1.35	4.09	9.5	81.6	1.61	3.62	3.8	29.8
400	60.9	1.36	4.11	9.7	81.9	1.62	3.63	3.9	29.5
600	60.9	1.36	4.11	9.6	82.1	1.62	3.63	3.9	29.3
800	61.0	1.36	4.09	9.7	82.2	1.62	3.63	4.0	29.0
1,000	60.9	1.37	4.11	10.0	82.0	1.62	3.61	3.9	28.8
1,200	60.7	1.37	4.11	10.0	81.9	1.63	3.62	4.0	28.6

(c) $CaSO_4$ (40°C)

Pressure	Ca^{2+}				SO_4^{2-}				V_W (Å^3)
	λ°_i	$f_{R\text{-}S}$	r_e (Å)	h	λ°_i	$f_{R\text{-}S}$	r_e (Å)	h	
1 atm	81.5	1.35	4.13	9.7	113.1	1.63	3.60	3.7	30.0
200 kg/cm^2	82.0	1.36	4.12	9.7	113.6	1.64	3.59	3.7	29.7
400	82.0	1.36	4.11	9.7	113.8	1.64	3.58	3.6	29.5
600	82.0	1.36	4.09	9.6	113.8	1.64	3.56	3.5	29.3
800	82.0	1.37	4.08	9.6	113.6	1.65	3.55	3.5	29.1
1,000	81.8	1.37	4.07	9.6	113.5	1.66	3.55	3.5	28.9
1,200	81.5	1.38	4.07	9.7	112.9	1.66	3.54	3.5	28.7

(d) $MgSO_4$ (25°C)

Pressure	Mg^{2+} $r_e=0.65$Å				SO_4^{2-}				V_W (Å^3)
	λ°_i	$f_{R\text{-}S}$	r_e (Å)	h	λ°_i	$f_{R\text{-}S}$	r_e (Å)	h	
1 atm	53.1	1.25	4.31	11.1	80.0	1.60	3.66	4.0	30.0
200 kg/cm^2	53.6	1.25	4.30	11.1	80.8	1.60	3.65	4.0	29.8
400	53.9	1.26	4.32	11.4	81.1	1.60	3.65	4.0	29.5
600	54.2	1.26	4.30	11.3	81.6	1.61	3.65	4.0	29.3
800	54.3	1.26	4.28	11.3	81.7	1.61	3.64	4.0	29.0
1,000	54.3	1.27	4.31	11.6	81.7	1.62	3.65	4.1	28.8
1,200	54.3	1.27	4.29	11.5	81.7	1.62	3.63	4.0	28.6

where f_1, f_2 and f_3 are the activity coefficients of M^{2+}, SO_4^{2-} and $M^{2+}\cdot SO_4^{2-}$, respectively. In the dilute solution, the activity coefficients, f_1 and f_2, are calculated from the Debye-Hückel limiting equation [7],

$$-\log f_i = z_i^2 \frac{1.291\times 10^6}{(DT)^{3/2}} I^{1/2}, \tag{13}$$

where I is the ional concentration $\sum_i m_i z_i^2$, D the dielectric constant of water and T the absolute temperature, and the activity coefficient of $M^{2+}\cdot SO_4^{2-}$, f_3 is assumed to be unity. Using the Onsager theoretical equation[7] for the equivalent ionic conductance in the right of Eq. (5), we obtain

$$\Lambda = \alpha(\Lambda^\circ - 4S\sqrt{m\alpha}), \tag{14}$$

where S is the function of D, η° and Λ°. The values of α in Eq. (14) is solved by means of successive approximation. The dielectric constant of water at pressure P, $D^{(P)}$ is determined from the Owen-Brinkley equation [19],

$$1-\frac{D^{(1)}}{D^{(P)}} = AD^{(1)} \log\frac{B+P}{B+1}, \tag{15}$$

where A and B are characteristic parameters of water. The viscosity data are graphically interpolated values from the measurements of Cappi [11]. The dissociation constant K thus determined from Eqs. (12), (13) and (14) at each pressure and temperature are listed in Table 3.

The dissociation constant increases with increasing pressure at each temperature. When the dissociation constant of the ion-pair, $Ca^{2+}\cdot SO_4^{2-}$ is compared with that of the ion-pair, $Mg^{2+}\cdot SO_4^{2-}$ at

Table 3 Dissociation constants of the ion-pair

Pressure	$CaSO_4$ (15°C)	$CaSO_4$ (25°C)	$CaSO_4$ (40°C)	$MgSO_4$ (25°C)
1 atm	6.0×10^{-3}	4.9×10^{-3}	3.1×10^{-3}	5.8×10^{-3}
	5.3×10^{-3} (18°C)[a]	4.9×10^{-3}[b]	4.1×10^{-3}[c]	4.4×10^{-3}[e]
			3.4×10^{-3}[d]	6.2×10^{-3}[f]
200 kg/cm²	7.1×10^{-3}	5.0×10^{-3}	3.3×10^{-3}	6.7×10^{-3}
400	7.7×10^{-3}	5.5×10^{-3}	3.4×10^{-3}	7.4×10^{-3}
600	8.1×10^{-3}	5.8×10^{-3}	3.5×10^{-3}	7.5×10^{-3}
800	9.9×10^{-3}	6.3×10^{-3}	3.7×10^{-3}	7.7×10^{-3}
1,000	1.0×10^{-2}	7.3×10^{-3}	3.8×10^{-3}	8.1×10^{-3}
1,200	1.2×10^{-2}	8.0×10^{-3}	4.1×10^{-3}	8.7×10^{-3}

a) from conductivity [21] b) from solubility [22] c) from solubility [22]
d) from solubility [23] e) from e.m.f. [24] f) from conductivity [25]

19) B. B. Owen and S. R. Brinkley, *Phys. Rev.*, 64, 32 (1943)
20) K. W. Kunttz and R. M. Fuoss, *J. Phys. Chem.*, 67, 914 (1962)
21) C. W. Davies, *Trans. Faraday Soc.*, 23, 351 (1927)
22) R. P. Bell and J. H. George, *ibid.*, 49, 619 (1953)
23) A. W. Gardner and E. Gluekauf, *ibid.*, 66, 1081 (1970)
24) H. W. Jones and C. B. Monk, *ibid.*, 48, 929 (1952)
25) H. S. Dunsmore and J. C. James, *J. Chem. Soc.*, 1951, 2925

25°C, the former is smaller at each pressure. It was observed by Kuntz and Fuoss [20] that in NaCl, KCl and RbCl solutions, the larger the crystal radius of a cation is, the smaller the dissociation constant. Figs. 5 and 6 show the variation of $\log K$ with pressure and temperature, respectively. From these plots, the thermodynamic parameters concerning the dissociation of the ion-pair (Eq. (11)) were calculated from the following relations,

$$\Delta\bar{G}^\circ = -RT\ln K, \tag{16}$$

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta\bar{V}^\circ}{RT}, \tag{17}$$

$$\left(\frac{\partial \ln K}{\partial (1/T)}\right)_P = -\frac{\Delta\bar{H}^\circ}{R}, \tag{18}$$

$$\Delta\bar{S}^\circ = \frac{\Delta\bar{H}^\circ - \Delta\bar{G}^\circ}{T}. \tag{19}$$

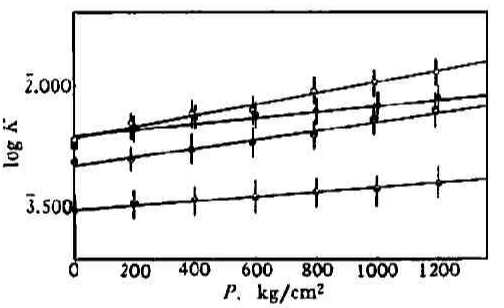

Fig. 5 $\log K$ *vs* P

○: $CaSO_4$, 15°C, ◓: $CaSO_4$, 25°C
◒: $CaSO_4$, 40°C, ●: $MgSO_4$, 25°C

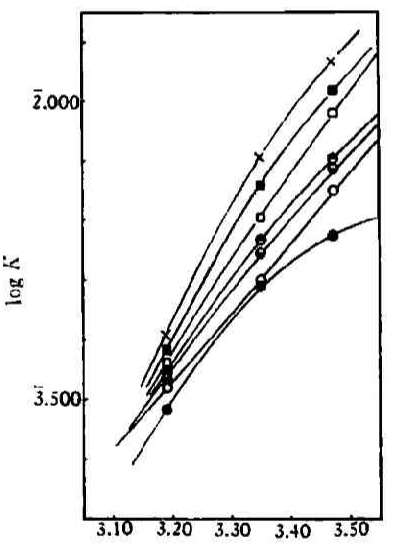

Fig. 6 $\log K$ *vs* $1/T$

●: 1 atm, ○: 200 kg/cm²
◓: 400 kg/cm², ◑: 600 kg/cm²
□: 800 kg/cm², ■: 1,000 kg/cm²
×: 1,200 kg/cm²

The derived thermodynamic parameters are given in Table 4. Our value of $\Delta\bar{V}^\circ$ in the dissociation of Mg^{2+}-SO_4^{2-} at 25°C, −7.7 cc/mole, is in good agreement with Fisher's value, -7.3 ± 0.4 cc/mole [26]. The negative values of $\Delta\bar{V}^\circ$, $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ would be due to the change of hydration number and the

26) F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962)

Table 4 Thermodynamic parameters concerned with the dissociation of the ion-pair

Pressure	$\Delta\bar{V}^\circ$ (ml/mole)				$\Delta\bar{H}^\circ$ (kcal/mole)	$\Delta\bar{G}^\circ$ (kcal/mole)	$\Delta\bar{S}^\circ$ (e.u.)
	$CaSO_4$ (15°C)	$CaSO_4$ (25°C)	$CaSO_4$ (40°C)	$MgSO_4$ (25°C)	$CaSO_4$	$CaSO_4$ (25°C)	$CaSO_4$ (25°C)
1 atm					−4.7	3.1	−26.2
200 kg/cm²					−5.4	3.1	−28.5
400					−5.7	3.1	−29.5
600	−12.9	−10.2	−5.7	−7.7	−5.8	3.0	−29.5
800					−6.8	3.0	−32.9
1,000					−7.1	2.9	−33.5
1,200					−7.4	2.9	−34.5

contraction of the hydrated molecules by the electrostriction in the dissociation process. The $|\Delta\bar{V}^\circ|$ of the dissociation of $Ca^{2+}\cdot SO_4^{2-}$ decreases with increasing temperature as in the case of $[Co(NH_3)_6]^{3+}\cdot SO_4^{2-}$ [5]. According to Mukerjee[27], the volume change ammounts to −56 cc/mole in the process of the dissolution of the salt $MgSO_4$ into water and perhaps the similar ammount would be expected for the salt, $CaSO_4$. But the value of $|\Delta\bar{V}^\circ|$, |−7.7 cc/mole| obtained in this experiment are far smaller than the value, |−56 cc/mole| mentioned above. This would indicate that the ion-pairs, $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$ are already hydrated to some extent and attract its surrounding water molecules with electrostrictive force. The $|\Delta\bar{V}^\circ|$ of the ion-pair, $Ca^{2+}\cdot SO_4^{2-}$ is larger than that of the ion-pair, $Mg^{2+}\cdot SO_4^{2-}$. It may be due to less hydration of $Ca^{2+}\cdot SO_4^{2-}$ than that of $Mg^{2+}\cdot SO_4^{2-}$.

The closest approach distance, a, is obtained by putting the dissociation constant in this experiment into the theoretical equation of Fuoss[28],

$$K=\frac{3000}{4\pi Na^3}\exp\left(-\frac{|z_+\cdot z_-|e^2}{aDkT}\right), \tag{20}$$

where k is the Boltzmann constant and N Avogadro's number. The results are listed in Table 5. At 40°C the closest approach distance gradually decreases with increasing pressure, but at other temperatures the systematic changes by pressure are not observed. The bulk dielectric constant was used for the calculation of the closest approach distance. In the vicinity of the ion, the dielectric constant would be smaller than that of bulk water, as the dipoles of the water molecules in the vicinity of the ion are oriented by electrostrictive force. Using the effective dielectric constant, the values of the closest approach distance wolud become larger than those in Table 5. Therefore, the closest approach distances at 15 and 25°C in aqueous solution would be larger than the sum of the crystal radii cited in Table 5 and also at 40°C those may be somewhat larger. Hence, the ion-pair may contain some water molecules between the cation and anion. This is in good agreement with the result by ultrasonic absorption [4]. The closest approach distance of the $Ca^{2+}\cdot SO_4^{2-}$ ion-pair is smaller than that of the $Mg^{2+}\cdot SO_4^{2-}$ ion-pair at 25°C at each pressure, in spite of the fact that the former has a larger sum of the

27) P. Mukerjee, *J. Phys. Chem.*, 65, 740 (1960)
28) R. M. Fuoss, *J. Am. Chem. Soc.*, 80, 5059 (1958)

Table 5 Changes in the closest approach distances by pressure

Pressure	a (Å)			
	$CaSO_4$ (15°C)	$CaSO_4$ (25°C)	$CaSO_4$ (40°C)	$MgSO_4$ (25°C)
1 atm	4.10	4.02	3.72	4.17
200 kg/cm²	4.21	3.95	3.71	4.26
400	4.22	3.97	3.68	4.29
600	4.19	3.95	3.65	4.23
800	4.34	3.97	3.63	4.19
1,000	4.35	4.03	3.60	4.17
1,200	4.42	4.10	3.60	4.19
Sum of the crystal radii		3.72		3.38

crystal radii. This corresponds to the larger value of $|\Delta\overline{V}^\circ|$ of the $Ca^{2+}\cdot SO_4^{2-}$ ion-pair than that of the $Mg^{2+}\cdot SO_4^{2-}$ ion-pair and to the smaller hydration number of Ca^{2+} than that of Mg^{2+}. These would mean that the $Ca^{2+}\cdot SO_4^{2-}$ ion-pair has less number of water molecules between the cation and anion than the $Mg^{2+}\cdot SO_4^{2-}$ ion-pair. The closest approach distance decreases with increasing temperature in $Ca^{2+}\cdot SO_4^{2-}$ ion-pair as in the case of $[Co(NH_3)_6]^{3+}\cdot SO_4^{2-}$. That is, the ion-pair would gradually approach to contact one with increasing temperature [29,30].

Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan

29) T. Ellingsen and J. Smid, *J. Phys. Chem.*, **73**, 2712 (1969)
30) J. H. Beard and P. H. Plesch, *J. Chem. Soc.*, **1964**, 4879